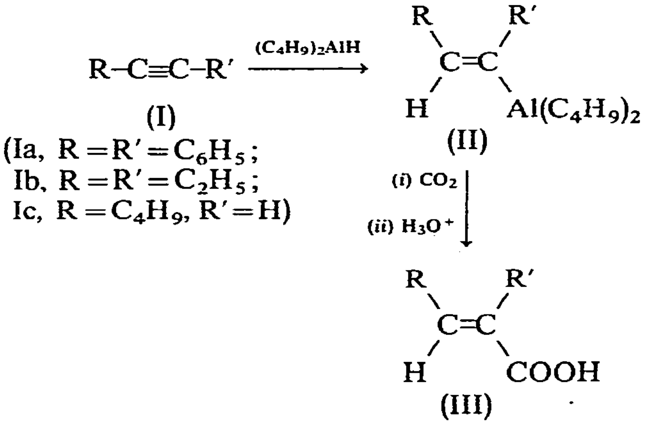
Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

PRELIMINARY COMMUNICATION

The carbonation of unsaturated organoaluminum compounds

Recent communications[1,2] on some reactions of methyllithium adducts of alkyl-substituted vinylaluminum compounds have prompted us to report our own findings bearing on the scope and limitations of the carbonation of vinylaluminum compounds themselves[3]. Thus, the addition of diisobutylaluminum hydrides to alkynes (I) occurs stereospecifically *cis*[4,5], to give vinylalanes (II), which with carbon dioxide directly undergo a preferential[*] reaction at the vinyl carbon–aluminum bond to give the corresponding acid (III) with complete retention of geometrical configuration:



(I)

(Ia, $R=R'=C_6H_5$;
Ib, $R=R'=C_2H_5$;
Ic, $R=C_4H_9$, $R'=H$)

(II)

(III)

In a typical experiment a solution of 0.056 mole of diphenylacetylene and 0.056 mole of diisobutylaluminum hydride in 100 ml of heptane was maintained at room temperature for 24 h and then at 50° for 4 h. Dry carbon dioxide gas was passed into the yellow solution without heating and the resulting reaction mixture was hydrolyzed with 2 *N* hydrochloric acid. A 96% yield of *cis*-α-phenylcinnamic acid, m.p. 177°, was obtained (based upon unrecovered alkyne). Gas chromatographic analysis of the methyl ester (via diazomethane) of the unrecrystallized acid showed it to be a single substance. Similarly, 3-hexyne and 1-hexyne gave the corresponding alkenoic acids (resultants of *cis*-hydrocarboxylation) in isolated yields of 60% and 35%, respectively. Thus, a convenient method for the stereospecific synthesis of alkenoic acids from terminal alkynes and symmetrical internal alkynes is at hand.

Attempts to prepare the *trans*-aluminum adducts by isomerizing the initially formed *cis*-vinylaluminum adducts (II) by heating (II) with diisobutylaluminum hydride[5] led to double bond migration with the 3-hexenyl system (IIb). A mixture of 2- and 3-hexenes resulted upon hydrolysis. The parallel isomerization attempt with

---

[*] *Cf.* ref. 6 for the carbonation of one carbon–aluminum bond in triethylaluminum.

the stilbenyl system (IIa) gave an 84:16 mixture of *trans*- and *cis*-stilbenes upon hydrolysis. In an unexpected fashion, however, this 84:16 mixture of *trans*- and *cis*-stilbenyl(diisobutyl)aluminums underwent carbonation at room temperature to yield 16% of the *cis*-α-phenylcinnamic acid (*ca.* quantitative), 8% of the *trans*-acid and *trans*-stilbene. Prolonged carbonation at 90° (8 h) yielded only 20% of *trans*-acid (analysis by GLC of methyl esters). These results reveal a unique case of striking rate differences for the carbonation of organometallic geometrical isomers. It is tempting to view the lower reactivity of the *trans*-stilbenylaluminum system as due to steric interference with a four-center transition state requiring copolanarity of the vinyl π-orbital and the available aluminum 3 *p*-orbital. Although such a view must be tested critically in further studies, the lower reactivity of *trans*-IIa in other reactions fits this interpretation.

Acknowledgements

We wish to express our appreciation to the Public Health Service for support of this research under Grant GM-13421.

Department of Chemistry
The Catholic University of America
Washington, D. C. 20017 (U.S.A.)

JOHN J. EISCH
MICHAEL W. FOXTON

1 G. ZWEIFEL AND R. B. STEELE, *J. Amer. Chem. Soc.*, 89 (1967) 5085.
2 G. ZWEIFEL AND R. B. STEELE, *J. Amer. Chem. Soc.*, 89 (1967) 2754.
3 J. J. EISCH AND M. W. FOXTON, *Amer. Chem. Soc. Maryland Meeting-in-Miniature*, May 5, 1967, Baltimore (Md.); *I.U.P.A.C. 3rd Intern. Symp. Organometal. Chem.*, September 1, 1967, Munich (Germany).
4 G. WILKE AND H. MÜLLER, *Chem. Ber.*, 89 (1956) 444.
5 J. J. EISCH AND W. C. KASKA, *J. Amer. Chem. Soc.*, 88 (1966) 2213.
6 K. ZIEGLER, F. KRUPP, K. WEYER AND W. LARBIG, *Ann. Chem.*, 629 (1960) 251.

Received October 6th, 1967